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(54) **Mechanochemical actuator**

(57) A mechanochemical actuator capable of producing mechanical energy in response to stimuli such as change in pH or salt concentration comprises a polymer composed of hydrophobic polymeric segments and hydrophilic polymeric segments, said hydrophobic polymeric segments being derived from either (1) a copolymer formed from a hydrophobic polymerizable monomer and a polymerizable monomer capable of forming hydrophilic polymeric segments after copolymerization with said hydrophobic polymerizable monomer and, if necessary, polymer modification, or (2) a modified product of said copolymer. Examples include a saponified product of an ethylene-acrylic acid copolymer or butadiene-acrylic acid copolymer, or a maleic acid-modified product of EPDM or polybutadiene, or a sulfone-modified product of EPDM or polybutadiene.

The actuator can be used in small machines (eg robots), medical appliances and prosthetic devices.

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FIG. 1

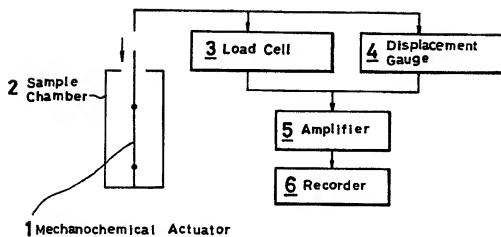
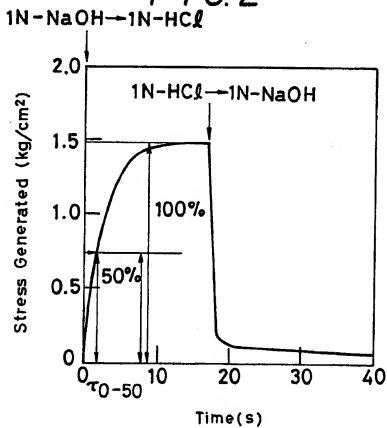


FIG. 2



MECHANOCHEMICAL ACTUATOR

The present invention relates to a mechanochemical actuator and, more particularly, to a high-strength mechanochemical actuator suitable for use as an actuator for small machines (such as robots) and medical appliances and prosthetic devices.

A mechanochemical actuator is a substance which generates mechanical energy upon receipt of chemical actions such as change in pH or salt concentration. It is expected to find use for small machines (such as robots) and medical appliances and prosthetic devices.

The mechanochemical actuator defined as above is made of a material which expands and contracts reversibly in response to external stimuli. Examples of such a material include methacrylic acid-vinyl alcohol copolymer and a mixture of poly-N-vinylpyrrolidone and polymethacrylic acid (which is water-insoluble owing to hydrogen bonds). A disadvantage of these materials is that they are so poor in elasticity that they are easily broken by shear stress.

There was proposed a mechanochemical actuator having improved mechanical strength in Japanese Patent Laid-open No. 228009/1986. This mechanochemical actuator is formed by polymerizing methacrylic acid after mixing with a

crosslinking agent in water or a water-ethanol mixed solvent, said crosslinking agent being represented by the formula $(CH_2=CHR-CO)_2X$ (where R is a hydrogen atom or alkyl group, and X denotes $-NHCH_2CH_2NH-$ or $-OCH_2CH_2O-$). The development of this mechanochemical actuator is based on an idea that the length of crosslinked parts in the material is responsible for the mechanical strength of a mechanochemical actuator.

There is known another high-strength mechanochemical actuator which was formed from polyacrylonitrile by pyrolytic crosslinking and subsequent hydrolysis to introduce the ionic structure. (Okui et al., Polymer Preprints, Japan, Vol. 36, No. 9 [1987])

A disadvantage of the former mechanochemical actuator (disclosed in Japanese Patent Laid-open No. 228009/1986) is that the hydrolysis after crosslinking is difficult to control and the resulting product is not uniform in the reversible stretching and contracting performance.

A disadvantage of the latter mechanochemical actuator (formed from polyacrylonitrile by pyrolytic crosslinking and subsequent hydrolysis to introduce the ionic structure) is that it has an extremely low strength in the swollen state.

The present invention was completed to address the above-mentioned problems associated with the conventional technology. Accordingly, the present invention aims

to provide a new mechanochemical actuator which has outstanding elasticity and hence extremely high strength in shear and exhibits very good reversible stretching and contracting performance in response to external stress.

The present invention also aims to provide a polymeric mechanochemical actuator which can be produced efficiently on account of the easy control of polymeric structure.

The present invention provides a mechanochemical actuator capable of producing mechanical energy in response to stimuli such as change in pH or salt concentration, said mechanochemical actuator comprising a polymeric substance composed of hydrophobic polymeric segments and hydrophilic polymeric segments, said hydrophobic polymeric segments being derived from either (1) a copolymer formed from a hydrophobic polymerizable monomer and a polymerizable monomer capable of forming hydrophilic polymeric segments after copolymerization with said hydrophobic polymerizable monomer and, if necessary, polymer modification, or (2) a modified product of said copolymer.

According to the present invention, the mechanochemical actuator is composed of hydrophobic polymeric segments and hydrophilic polymeric segments, the former functioning as the reinforcing layer which imparts strength to the mechanochemical actuator, and the latter inducing the reversible structural change which gives rise to the reversible stretching and contracting motion and retaining water which plays a part in the reversible structural change.

Because of this unique composition, the mechanochemical actuator of the present invention has high strength and exhibits good response performance.

Moreover, the mechanochemical actuator of the present invention has a polymeric structure which can be controlled very easily in the manufacturing process because it is made of a polymeric substance which is a copolymer composed of a hydrophobic monomer and a reactive hydrophobic monomer and/or hydrophilic monomer, or a modified product of said copolymer.

By way of example, embodiments of the invention will now be described. In the drawings:

Fig. 1 is a schematic system diagram of an apparatus used to measure the stress generated and the stretching and contracting strokes in Examples and Comparative Examples; and

Fig. 2 is a graph showing a stimulus response curve.

The invention will be fully described in the following. In this specification, the term "reactive hydrophobic polymerizable monomer" means a hydrophobic polymerizable monomer which imparts the hydrophilic nature upon polymer modification.

According to the present invention, the mechanochemical actuator is made of a binary copolymer, a ternary copolymer, or a modified product thereof. The binary copolymer is composed of two kinds of monomers selected from a group consisting of a hydrophobic polymerizable monomer, a reactive hydrophobic polymerizable monomer, and a hydrophilic polymerizable monomer. The ternary copolymer is composed of said three monomers. The modified product is produced by making the reactive hydrophobic polymeric segments hydrophilic partially or entirely.

In other words, the mechanochemical actuator of the present invention is made of any one of the following polymeric substances (1) to (6), each composed of hydrophobic polymeric segments and hydrophilic polymeric segments.

- (1) A copolymer composed of a hydrophobic polymerizable monomer and a hydrophilic polymerizable monomer.

(2) A modified product of a copolymer composed of a hydrophobic polymerizable monomer and a reactive hydrophobic polymerizable monomer.

(3) A copolymer composed of a reactive hydrophobic polymerizable monomer and a hydrophilic polymerizable monomer.

(4) A partially modified product of a copolymer composed of a reactive hydrophobic polymerizable monomer and a hydrophilic polymerizable monomer.

(5) A ternary copolymer composed of a hydrophobic polymerizable monomer, a reactive hydrophobic polymerizable monomer, and a hydrophilic polymerizable monomer.

(6) A modified product of a ternary copolymer composed of a hydrophobic polymerizable monomer, a reactive hydrophobic polymerizable monomer, and a hydrophilic polymerizable monomer.

In the mechanochemical actuator of the present invention, the hydrophobic polymeric segments function as a reinforcing layer which makes the mechanochemical actuator very strong.

According to the present invention, the hydrophobic polymerizable monomer includes one or more members selected from ethylene, propylene, styrene, butadiene, isoprene, chloroprene, vinyl chloride, fluorocalkylene, *i*-butylene, butene, siloxane, etc.

The hydrophobic polymeric segments to be formed by polymerization should preferably be crystalline segments (such as polyethylene) or crosslinkable segments (such as polybutadiene and polyisoprene).

The reactive hydrophobic polymerizable monomer, which forms the hydrophilic polymeric segments by modification after polymerization, includes one or more members selected from ethylene halide (such as vinyl chloride), diene derivative (such as cyanoprene), halogenated styrene derivative (such as p-chlorostyrene), acrylic ester (such as methyl acrylate and ethyl acrylate), methacrylic ester (such as methyl methacrylate and ethyl methacrylate), acrylonitrile, methacrylonitrile, etc.

In the mechanochemical actuator of the present invention, the hydrophilic polymeric segments induce the reversible structural change which gives rise to the reversible stretching and contracting motion and retains water which plays a part in the reversible structural change.

Therefore, the hydrophilic polymeric segments in the mechanochemical actuator of the present invention should be formed from a monomer of ionic structure or nonionic structure. A monomer of ionic structure is introduced for the reversible structural change and the water retaining performance owing to its high water absorptivity. A

monomer of nonionic structure is introduced for the water retaining performance alone owing to its low water absorptivity.

Examples of the monomer of ionic structure include ammonium salts and phosphonium salts (which are of cationic structure), and carboxylic acids and metal salts thereof, metal sulfonates, and phosphoric acid and salts thereof (which are of anionic structure). Examples of the monomer of nonionic structure include ethylene glycol, vinyl alcohol, and acrylamide derivatives.

Examples of the mechanochemical actuator of the present invention include the following.

- (1) A saponified product of a copolymer composed of ethylene and acrylic acid and/or acrylic ester.
- (2) A saponified product of a copolymer composed of butadiene and acrylic acid and/or acrylic ester.
- (3) A maleic acid-modified product of ethylene-propylene-diene terpolymer (EPDM) or polybutadiene.
- (4) A sulfone-modified product of EPDM or polybutadiene.

The one belonging to category (1) above may be composed of, for example, ethylene and ethyl acrylate in a ratio (by weight) of 40/60 to 99.5/0.5, preferably 50/50 to 99/1, and most desirably 60/40 to 98/2. With ethyl acrylate less than 0.5 wt%, the resulting mechanochemical

actuator is very poor in the reversible stretching and contracting performance. With ethyl acrylate more than 60 wt%, the resulting mechanochemical actuator does not have the sufficient crystalline structure necessary for reinforcement on account of the incomplete copolymerization of ethylene with ethyl acrylate.

The one belonging to category (2) above may be composed of, for example, butadiene and ethyl acrylate in a ratio (by weight) of 40/60 to 99.5/0.5, preferably 50/50 to 99/1, and most desirably 60/40 to 98/2. With ethyl acrylate less than 0.5 wt%, the resulting mechanochemical actuator is very poor in the reversible stretching and contracting performance. With ethyl acrylate more than 60 wt%, the resulting mechanochemical actuator does not have the sufficient crystalline structure necessary for reinforcement.

The one belonging to category (3) above may be composed of, for example, EPDM and maleic anhydride in a ratio (by weight) of 40/60 to 99.5/0.5, preferably 50/50 to 99/1, and most desirably 60/40 to 98/2. With maleic anhydride less than 0.5 wt%, the resulting mechanochemical actuator is very poor in the reversible stretching and contracting performance. With maleic anhydride more than

60 wt%, the resulting mechanochemical actuator does not have the sufficient crystalline structure necessary for reinforcement.

The one belonging to category (3) above may also be composed of, for example, polybutadiene and maleic anhydride in a ratio (by weight) of 40/60 to 99.5/0.5, preferably 50/50 to 99/1, and most desirably 60/40 to 98/2. With maleic anhydride less than 0.5 wt%, the resulting mechanochemical actuator is very poor in the reversible stretching and contracting performance. With maleic anhydride more than 60 wt%, the resulting mechanochemical actuator does not have the sufficient crystalline structure necessary for reinforcement.

The one belonging to category (4) above may be composed of, for example, EPDM and *p*-styrenesulfonic acid in a ratio (by weight) of 25/75 to 99/1, preferably 30/70 to 98/2, and most desirably 40/60 to 96/4. With *p*-styrenesulfonic acid less than 1 wt%, the resulting mechanochemical actuator is very poor in the reversible stretching and contracting performance. With *p*-styrenesulfonic acid more than 75 wt%, the resulting mechanochemical actuator does not have the sufficient crystalline structure necessary for reinforcement.

The one belonging to category (4) above may also be composed of, for example, polybutadiene and *p*-styrenesulfonic acid in a ratio (by weight) of 25/75 to 99/1, preferably 30/70 to 98/2, and most desirably 40/60 to 96/4. With *p*-styrenesulfonic acid less than 1 wt%, the resulting mechanochemical actuator is very poor in the reversible stretching and contracting performance. With *p*-styrenesulfonic acid more than 75 wt%, the resulting mechanochemical actuator does not have the sufficient crystalline structure necessary for reinforcement.

The mechanochemical actuator of the present invention may be composed of the above-mentioned polymeric substances alone; but it may be incorporated with a reinforcing agent and crosslinking agent for the further improvement of strength, or with a water retaining agent to prevent drying.

Examples of the reinforcing agent include polyethylene, polypropylene, and polyvinyl chloride.

Examples of the crosslinking agent (curing agent) include sulfur, peroxide, *N*, *N'*-methylenebisacrylamide, *N*, *N'*-methylenebismethacrylamide, and 1,3-diacrylamide-methyl-2-imidazoline. (Crosslinking by electron rays or radiation may also be possible.)

Examples of the water retaining agent include cellulose, methyl cellulose, polyvinylalcohol, polyethylene glycol, and copolymers thereof with 2-hydroxyethyl methacrylate, 2-hydroxypropyl methacrylate, and acrylamide.

These additives should preferably be added in an amount of 2 to 30 wt% of the above-mentioned polymeric substance.

The mechanochemical actuator of the present invention derives its reversible stretching and contracting force from the movement of the water adsorbed by the polymeric substance constituting it. The rate of the reversible stretching and contracting motion depends on the diffusion rate of the water. For the mechanochemical actuator to effectively exhibit its reversible stretching and contracting performance, it is necessary that the mechanochemical actuator have a very large surface area. For this reason, the mechanochemical actuator of the present invention should preferably be in the form of filament or film with a surface of porous or microstructure.

The mechanochemical actuator of the present invention may be produced easily in the usual way from the above-mentioned polymeric substance incorporated with optional additives.

As mentioned above, the mechanochemical actuator of the present invention has superior elasticity and high strength in shear and exhibits very good reversible stretching and contracting performance in response to stress. In addition, it can be produced efficiently with easy control of its polymer structure.

The invention will be described with reference to the following examples and comparative examples, which are not intended to restrict the scope of the invention.

Example 1

In 90 g of toluene was dissolved 10 g of commercial ethylene-ethyl acrylate (EEA) ("NUC-6570" made by Nippon Unicar Co., Ltd.) with heating at 90°C. To the resulting toluene solution was added 20 g of methanol solution containing 5 g of sodium hydroxide. After thorough stirring, the solution was allowed to stand for two days to effect reactions. The reaction product was filtered out, followed by rinsing and vacuum-drying. The saponified EEA thus obtained was made into a sheet by hot-pressing. This sheet was immersed in water until it was swollen and equilibrated and then tested for physical properties in the following manner. The results are shown in Table 1.

Tensile test

A test piece (conforming to JIS No. 1) was punched out of the sheet, and it was tested for strength at break and elongation at break according to the method provided in JIS K-6301. The pulling rate was 100 mm/min.

Stress and stretching and contracting strokes

The performance of the mechanochemical actuator was evaluated by measuring the response to pH change which takes place when the environment is changed from a 1N-NaOH aqueous solution to a 1N-HCl aqueous solution. The apparatus used for measurements is shown in Fig. 1 which is a schematic system diagram. The apparatus is made up of a sample chamber 2 in which is placed the sample of mechanochemical actuator 2, a load cell 3, a displacement gauge 4, an amplifier 5, and a recorder 6. A response curve obtained with this apparatus is shown in Fig. 2. The rate of response is expressed in terms of time (τ_{0-50}) required for the mechanochemical actuator to undergo 50% of the displacement. (The 100% displacement is the difference between the length (l_{max}) of the mechanochemical actuator in the stretched equilibrium and the length (l_{min}) of the mechanochemical actuator in the contracted equilibrium.)

Example 2

The same procedure as in Example 1 was repeated except that the EEA was replaced by a commercial EEA ("MB-870" made by Nippon Unicar Co., Ltd.). The results are shown in Table 1.

Comparative Example 1

A sample was prepared according to the process shown in Japanese Patent Laid-open No. 228009/1986 (Example 1). The sample was tested in the same manner as in Example 1. The results are shown in Table 1.

Comparative Example 2

A fibrous sample of mechanochemical actuator was prepared from polyacrylonitrile fiber (made by Asahi Chemical Industry Co., Ltd.) by pyrolytic crosslinking at 220°C for 2 hours and subsequent saponification for 2 hours with a saturated methanol solution of sodium hydroxide. This sample was tested for stress and stretching and contracting strokes in the same manner as in Example 1. The results are shown in Table 1.

It is noted from Table 1 that the mechanochemical actuator of the present invention has good elasticity and an extremely high strength and is superior in that the stress in a constant length is well-balanced with the stretching and contracting strokes under a constant load.

Table 1

Items	Example 1	Example 2	Comparative Example 1	Comparative Example 2
Tensile strength at break ($\text{kg}\cdot\text{cm}^{-2}$)	52.7	20.0	1.0 *	—
Elongation at break (%)	110	300	260 *	—
Stress at constant length ($\text{kg}\cdot\text{cm}^{-2}$)	1.5	1.0	— ***	20.0
Stretching and contracting strokes under constant load ($l_{\text{max}}/l_{\text{min}}$) **	1.1	1.4	— ***	1.01
Response time ($\tau_{0.90}$) (s)	2.0	1.0	— ***	1.0

- * Measured when the sample was prepared (before swelling)
 ** l_{max} denotes the length of the mechanochemical actuator in stretched equilibrium, and l_{min} denotes the length of the mechanochemical actuator in contracted equilibrium.
 *** Unmeasurable.

CLAIMS:

1. A mechanochemical actuator capable of producing mechanical energy in response to stimuli such as change in pH or salt concentration, said mechanochemical actuator comprising a polymeric substance composed of hydrophobic polymeric segments and hydrophilic polymeric segments; said hydrophobic polymeric segments being derived from either (1) a copolymer formed from a hydrophobic polymerizable monomer and a polymerizable monomer capable of forming hydrophilic polymeric segments after copolymerization with said hydrophobic polymerizable monomer and, if necessary, polymer modification, or (2) a modified product of said copolymer.

2. A mechanochemical actuator as claimed in Claim 1, which is made of a binary copolymer, a ternary copolymer, or a modified product thereof, said binary copolymer being composed of two kinds of monomers selected from a group consisting of a hydrophobic polymerizable monomer, a reactive hydrophobic polymerizable monomer which eventually becomes hydrophilic after modification, and a hydrophilic polymerizable monomer, said ternary copolymer being composed of said three monomers, and said modified product being produced by making the reactive hydrophobic polymeric segments hydrophilic partially or entirely after polymerization.

3. A mechanochemical actuator as claimed in Claim 2, which is made of one of the following polymeric substances (1) to (6) and contains hydrophobic polymeric segments and hydrophilic polymeric segments.

(1) A copolymer composed of a hydrophobic polymerizable monomer and a hydrophilic polymerizable monomer.

(2) A modified product of a copolymer composed of a hydrophobic polymerizable monomer and a reactive hydrophobic polymerizable monomer.

(3) A copolymer composed of a reactive hydrophobic polymerizable monomer and a hydrophilic polymerizable monomer.

(4) A partially modified product of a copolymer composed of a reactive hydrophobic polymerizable monomer and a hydrophilic polymerizable monomer.

(5) A ternary copolymer composed of a hydrophobic polymerizable monomer, a reactive hydrophobic polymerizable monomer, and a hydrophilic polymerizable monomer.

(6) A modified product of a ternary copolymer composed of a hydrophobic polymerizable monomer, a reactive hydrophobic polymerizable monomer, and a hydrophilic polymerizable monomer. ;

4. A mechanochemical actuator as claimed in Claim 3, wherein the hydrophobic polymerizable monomer is one or more than one member selected from the group consisting of

ethylene, propylene, styrene, butadiene, isoprene, chloroprene, vinyl chloride, fluoroalkylene, i-butylene, butene, and siloxane.

5. A mechanochemical actuator as claimed in Claim 3, wherein the reactive hydrophobic polymerizable monomer is one or more than one member selected from the group consisting of ethylene halide, diene derivative, halogenated styrene derivative, acrylic ester, methacrylic ester, acrylonitrile, and methacrylonitrile.

6. A mechanochemical actuator as claimed in Claim 1, wherein the hydrophilic polymeric segments are made of a monomer of ionic structure with high water absorptivity or a monomer of nonionic structure with low water absorptivity.

7. A mechanochemical actuator as claimed in Claim 6, wherein the monomer of ionic structure with high water absorptivity is selected from ammonium salts and phosphonium salts (which are of cationic structure), and carboxylic acids and metal salts thereof, metal sulfonates, and phosphoric acid and salts thereof (which are of anionic structure).

8. A mechanochemical actuator as claimed in Claim 6, wherein the monomer of nonionic structure with low water absorptivity is selected from ethylene glycol, vinyl alcohol, and acrylamide derivatives.

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9. A mechanochemical actuator as claimed in Claim 1, whose major constituent is one of the following.

(1) A saponified product of a copolymer composed of ethylene and acrylic acid and/or acrylic ester.

(2) A saponified product of a copolymer composed of butadiene and acrylic acid and/or acrylic ester.

(3) A maleic acid-modified product of ethylene-propylene-diene terpolymer (EPDM) or polybutadiene.

(4) A sulfone-modified product of EPDM or polybutadiene.

10. A mechanochemical actuator as claimed in Claim 9, which is composed of ethylene and ethyl acrylate in a ratio of 40/60 to 99.5/0.5 (by weight).

11. A mechanochemical actuator as claimed in Claim 1, which has the surface of porous or microstructure.

12. A mechanochemical actuator substantially as hereinbefore described in Example 1 or Example 2.

13. A mechanochemical actuator as claimed in Claim 1, substantially as hereinbefore described and with reference to the drawings.